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Mineralisation of Monuron photoinduced by Fe(III) in aqueous solution

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Abstract

The degradation of Monuron (3-(4-chlorophenyl)-1,1-dimethylurea) photoinduced by Fe(III) in aqueous solution has been investigated. The rate of degradation depends on the concentration of $Fe(OH)^{2+}$, the most photoreactive species in terms of 'OH radical formation. These 'OH radicals are able to degrade Monuron until total mineralisation. The primordial role of the speciation of Fe(III)-hydroxy complex in aqueous solution, for the efficiency of the elimination of pollutant, was shown and explained in detail. The formation of Fe(II) in the irradiated solution was monitored and correlated with the total organic carbon evolution. Degradation photoproducts were identified and a mechanism of degradation is proposed.

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1. Introduction

The intensive use of pesticides on large areas of agricultural soil has given rise to concern about their fate in the environment. Less than 1% of total applied pesticides reach the target pests, the vast majority being dispersed in the different environmental compartments of the environment but mainly in aquatic environment via agricultural runoff or leaching. Thus, pesticides are among the most frequently occurring organic pollutants in natural waters. Great care has been developed about possible processes that pesticides might undergo when they are dispersed in the environment. Among the different abiotic degradation processes, solar irradiation is one of the main factors responsible for pollutant degradation in aquatic environment (Faust, 1999). When the pollutant does not absorb solar light, its degradation can be photoinduced by radicals generated by different species, like Fe(III) aquocomplexes, presented or added in the aquatic compartment.

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Among pesticides, phenylurea derivatives are widely used as herbicides because of their inhibition of photosynthesis (Bucha and Todd, 1951), for general weed control of non-crop area and as pre-emergence on fruit crops. These herbicides have received a special attention in recent years because of their toxicity and possible carcinogenic properties. Several weeks, even months, are required for their removal from environment (White-Stevens, 1971; Mackay et al., 1997). This work is focused on the particular case of Monuron (3-(4-chlorophenyl)-1,1-dimethylurea). The life times of Monuron in the different compartments of environment were found to be relatively long; greater than 8 weeks in river waters (Eichelberger and Lichtenberg, 1971) and the half-life is equal to 170 days in the soil (Augustin-Beckers et al., 1994).

Several authors have investigated the degradation of Monuron. Two main ways of biodegradation are depicted in the literature for the *N*-aryl-*N'*,*N'*-dimethylurea derivatives. The first one is the hydrolysis of amide (Kearney, 1965) whereas the second is the *N*-demethylation (Tillmanns et al., 1978). Then, the phototransformation of Monuron has been the subject of several papers. Direct photolysis of Monuron has been studied in water under solar and UV irradiations (Hill et al., 1955; Weldom and Timmons, 1961). Crosby and Tang (1969) identified different photoproducts and proposed a mechanism of phototransformation. The photocatalytic degradation of Monuron with TiO₂ was also investigated in detail (Augugliaro et al., 1993; Pramauro et al., 1993).

Fe(III)-aquo complexes are known to undergo a photoredox process through an internal electron transfer yielding Fe(II) and hydroxyl radical (reaction (1)):

$$\operatorname{Fe}(\operatorname{III}) \xrightarrow{h\nu}_{H_2O} \operatorname{Fe}(\operatorname{II}) + \operatorname{HO}^{\bullet} + \operatorname{H}^+$$
(1)

Among the Fe(III)-aquo complexes, Fe(OH)²⁺ is the most photoreactive species in terms of hydroxyl radical formation (Benkelberg and Warneck, 1995). The percentage of Fe(OH)²⁺ (Fe(OH)²⁺ refers to Fe(OH) $(H_2O)_5^{2+}$) in iron(III) aqueous solution is influenced by many factors. The hydrolysis of iron(III) is a complex phenomena and many equilibria lead to numerous species (Flynn, 1984; Faust and Hoigné, 1990). However, the hydrolysis mainly depends on pH, initial concentration of Fe^{III}, temperature, ionic strength and nature of anions (Sylva, 1972).

Such systems, based on Fe(III) aquacomplexes as a source of OH radicals were proved to be efficient to induce the complete mineralisation of pollutants (Mailhot et al., 2002). In addition, due to its redox properties, iron can interfere with the different intermediates generated all along the process. In terms of wastewater treatment, such a process could be very useful in pre-treatment before a biological treatment with the goal of achieving the complete mineralisation of bio-recalcitrant pollutants (Sarria et al., 2003).

The present paper deals with Monuron degradation photoinduced by Fe(III) aquacomplexes until its complete mineralisation. The major photoproducts have been identified and a mechanism of Monuron degradation is proposed. A special emphasis is given to the role of the different Fe(III) species.

2. Experimental

2.1. Reagents and solutions

All reagents were of the purest grade commercially available and were used without further purification.

Monuron (3-(4-chlorophenyl)-1-1-dimethylurea) (99%) and 8-hydroxyquinoline-5-sulfonic acid monohydrate (HQSA; 98%) were purchased from Aldrich and used as received. Ferric perchlorate nonahydrate (Fe(ClO₄)₃, 9H₂O; >97%) was a Fluka product kept in a dessicator. Solutions of Fe(III) used for the studies (3×10^{-4} moll⁻¹), were prepared by diluting stock solutions of Fe(ClO₄)₃, 9H₂O (2.0×10^{-3} moll⁻¹) to the appropriate Fe(III) concentration. 2-Propanol and acetonitrile were HPLC grade products and purchased from Merck and Carlo Erba respectively. For the synthesis of authentic samples of photoproducts, 4-chlorophenyl isocyanate (98%), methylamine (2M in THF solution) and *N*-methylformamide (99%) were Aldrich products.

All solutions were prepared with deionized ultra pure water ($\rho = 18.2 \,\mathrm{M\Omega cm}$). When necessary, the solutions were deoxygenated at room temperature either by argon bubbling for 30 min in 5 ml quartz cell or by continuous nitrogen bubbling in the reactor used for irradiation (100 ml). We checked that there was no elimination of Monuron during the bubbling. The pH was measured with an Orion pH-meter to ± 0.1 pH unit (pH = 3.3 for a solution with a concentration in Fe(III) equal to $3.0 \times 10^{-4} \,\mathrm{M}$). The ionic strength was not controlled.

2.2. Apparatus

In order to measure the quantum yields, monochromatic irradiations at 296, 313, 334 and 365 nm were carried out with a high-pressure mercury lamp (Osram HBO 200 W) equipped with a monochromator (Bausch and Lomb) providing a parallel beam. The reactor was a cylindrical quartz cell of 2 cm path length. The light intensity was measured by ferrioxalate actinometry (Calvert and Pitts, 1966) (Table 1). The quantum yields were calculated for a reaction extent lower than 10%.

In order to irradiate larger volume (V = 60 ml) at $\lambda_{\text{exc.}} = 365$ nm, for kinetic and analytical experiments, an elliptical stainless steel reactor was used. A high-pressure

Table 1

Photonic flux and initial quantum yields of Monuron disappearance as a function of irradiation wavelength

λ (nm)	296	313	334	365
I ₀	5.6×10^{14}	1.00×10^{15}	6.4×10^{14}	2.12×10^{15}
$(photons s^{-1} cm^{-2})$				
$\Phi_{ m Monuron}$	0.121	0.109	0.106	0.025

 $[Fe(III)]_0 = 3.0 \times 10^{-4} \text{moll}^{-1}$ (90% of monomeric species) and $[Monuron]_0 = 4.0 \times 10^{-4} \text{moll}^{-1}$.

mercury lamp enclosed in a glass filter bulb (Mazda HPW type 125 W), whose emission consists of 93% at 365 nm (few percents of the light is emitted at 313, 334 and 405 nm), was placed in one of the focal axes, while the photoreactor, a water-jacketed Pyrex tube (internal diameter = 2.8 cm), was centred at the other one. The reaction medium was continuously stirred.

UV-visible spectra were recorded on a Cary 3 double beam spectrophotometer.

HPLC experiments were carried out using a Waters chromatograph equipped with two pumps Waters 510, an auto-sampler 717 and a Waters 996 photodiode array detector. The flow rate was 1 ml min⁻¹ and the eluent a mixture of pure water and acetonitrile (v/v 70/30). The column was a Lichrosphere (Merck) RP18 (reverse phase) of $125 \times 4.6 \text{ mm}$ with a particle diameter of 5µm and a pore diameter of 100 Å.

The purity of synthesised authentic photoproducts was checked by NMR. ¹H and ¹³C spectra were recorded on a Bruker Avance DSX spectrometer operating at 300.13 MHz for the proton. The mass spectra were obtained using a Hewlett-Packard model 5989B detector.

2.3. Analysis

The method of measuring the monomeric concentration of Fe(III) (mainly Fe(OH)²⁺ in our experimental conditions) was modified from Kuenzi's procedure (Kuenzi, 1982) and described in our previous papers (Brand et al., 1998; Mailhot et al., 1999). The measurement is based on the formation of the complex Fe(HQS)₃ between 8-hydroxyquinoline-5-sulfonic acid (HQSA) and Fe(III) monomeric species which presents a maximum absorption at 572 nm with a molar absorption coefficient equal to 50751mol⁻¹ cm⁻¹ (Mailhot et al., 1999).

Fe(II) concentration was determined by complexometry with *ortho*-phenanthroline, using $\varepsilon_{510} = 1.118 \times 10^{4} 1 \text{mol}^{-1} \text{ cm}^{-1}$ for the Fe(II)-phenanthroline complex (Calvert and Pitts, 1966).

The concentrations of Monuron and its photoproducts were followed by HPLC analysis ($\lambda_{detection} = 244 \text{ nm}$). Total Organic Carbon (TOC) measurements, based on the combustion of carbon detected by infrared gas analysis method, were followed with a TOC analyser Shimadzu (model TOC-5050A). The calibration curves within the range $1-20 \text{ mgl}^{-1}$ were obtained by using potassium hydrogen phthalate for total organic carbon and a mixture of sodium hydrogen carbonate and sodium carbonate for inorganic carbon. The threshold of detection is around 1.5 mgl^{-1} .

3. Results and discussion

3.1. Dark experiments

In our experimental conditions ([Fe(III)] = 3×10^{-4} M and pH = 3.4 ± 0.1), Fe(OH)²⁺ was the predominant monomeric Fe(III)-hydroxy complex (Benkelberg and Warneck, 1995), but its concentration rapidly decreased due to hydrolysis and oligomerisation processes leading to the formation of soluble aggregates. These processes control the proportion between the various Fe(III) species that differ in their photoactivities and thus influence the rate of hydroxyl radical production (Helz et al., 1994). The initial concentration of Fe(OH)²⁺ and the kinetics of its disappearance is strongly affected by the age of the stock solution (Krýsová et al., 2003). For this reason it is necessary to determine the percentage of Fe(OH)²⁺ before each experiment by the HQSA method (see Section 2.3).

% Fe(OH)²⁺ =
$$\frac{[Fe(OH)^{2+}]}{[Fe(III)]t_o} \times 100$$

where $[Fe(III)]t_o$ is the starting concentration of total Fe(III).

The solubility of Monuron in water at 25 °C is equal to 230 mgl^{-1} (1.16 × $10^{-3} \text{ moll}^{-1}$) (Mackay et al., 1997). A stock solution of $10^{-3} \text{ moll}^{-1}$ concentration was prepared by stirring during 48 h.

Cl---NH--C-N
$$CH_3$$
 Monuron (MW = 198.65 g mol⁻¹)

Unless otherwise noted, a concentration of 1.0×10^{-4} moll⁻¹ was used all along this work. Monuron was stable in aqueous solution; no degradation was observed in the dark and at room temperature after three months. The UV-visible spectrum of Monuron comprises one maximum at 244 nm ($\varepsilon = 180001$ mol⁻¹ cm⁻¹) and no absorbance at wavelength greater than 300 nm.

The mixture Monuron/Fe(III) in our experimental conditions was thermally stable (in the dark and at room temperature) in terms of Monuron concentration. So

Table 2 Influence of the monomeric species concentration and oxygen on the initial quantum yield of Monuron disappearance

[Monuron]	% Fe(OH) ²⁺	20%	40%	60%	90%	60% without O_2
$\begin{array}{c} 1.0 \times 10^{-4} \text{moll}^{-1} \\ 4.0 \times 10^{-4} \text{moll}^{-1} \end{array}$	$\Phi_{ m Monuron} \ \Phi_{ m Monuron}$	0.0023 0.0022	0.0060 0.0052	0.0103 0.0108	0.025 0.025	0.013
	4	1				

 $\lambda_{\text{irr.}} = 365 \,\text{nm}$ and $[\text{Fe(III)}]_0 = 3.0 \times 10^{-4} \,\text{mol}\,\text{l}^{-1}$.

there is no precipitation or redox reaction in this system. Moreover, no change either in concentration of $Fe(OH)^{2+}$ or in its disappearance kinetics was observed in the presence of Monuron. These results confirm the absence of interactions between Monuron and Fe(III) in aqueous solution kept in the dark.

3.2. Photodegradation of Monuron

Unless otherwise noted, Monuron $(1.0 \times 10^{-4} \text{ moll}^{-1})$ and Fe(III) $(3.0 \times 10^{-4} \text{ moll}^{-1})$ were the concentrations used all along this work. The kinetics of photodegradation were performed at 365 nm. This wavelength is sufficiently energetic to cause the photoredox process of Fe(III) aquacomplexes and it is present in solar spectrum. During the irradiation of the mixture, the concentration of Monuron continuously decreased.

3.2.1. Primary stage of the degradation

(a) Influence of the monomeric species concentration. The initial quantum yields of Monuron disappearance and Fe(II) formation are gathered in Tables 2 and 3 respectively. The results showed that the quantum yields of Monuron disappearance and Fe(II) formation were strongly dependent on the Fe(OH)²⁺ percentage: higher is the percentage, higher were the quantum yields of Monuron disappearance and Fe(II) formation. These results are directly linked to the nature of Fe(III)-hydroxo species present in solution and give evidence for the importance of Fe(III) speciation: Fe(OH)²⁺ is the most photoactive species in terms of OH radicals production (Faust and Hoigné, 1990; Benkelberg and Warneck, 1995) and consequently for Fe(II) formation and the degradation of the organic compound present in solution. The quantum yields of Fe(II) formation are always higher than the quantum yields of Monuron degradation. This result may be due to the rapid formation of photoproducts and after a competition for the reaction of hydroxyl radical.

(b) Influence of Monuron concentration. The effect of Monuron concentration on the photochemical reaction $(\lambda = 365 \text{ nm})$ was investigated for two concentrations in Monuron $(1.0 \times 10^{-4} \text{ mol}1^{-1} \text{ and } 4.0 \times 10^{-4} \text{ mol}1^{-1})$ with different percentage of Fe(III) monomeric species (Table 2). The initial quantum yields of Monuron disappear-

Table 3

Initial quantum yields of Fe(II) formation as a function of the percentage of monomeric species and oxygen

% Fe(OH) ²⁺	45%	60%	90%	60% without O_2
$\Phi_{\rm Fe(II)}$	0.0054	0.017	0.063	0.014
	10-4	11-1 0		1 10 10-4 11-1

[Fe(III)]₀ = 3.0×10^{-4} moll⁻¹, [Monuron]₀ = 1.0×10^{-4} moll⁻¹; $\lambda_{\text{irr.}} = 365$ nm.

ance are not affected by the starting Monuron concentration.

(c) Influence of the irradiation wavelength. In this set of experiments, the solutions of ferric perchlorate $(3.0 \times 10^{-4} \text{ moll}^{-1}, 90\%$ of monomeric species) and Monuron $(4.0 \times 10^{-4} \text{ moll}^{-1})$ were irradiated at 296, 313, 334 and 365 nm. The quantum yields of Monuron disappearance are given in Table 1. The quantum yield is significantly higher at 334 nm than at 365 nm and slightly increases at shorter wavelengths. This effect has to be related to the increase of the quantum yield of OH radical formation when the excitation wavelength decreases. It is consistent with the notion that ejection of OH radical from the solvent cage requires kinetic energy (Benkelberg and Warneck, 1995).

(d) Oxygen effect. The initial quantum yields of Monuron disappearance and Fe(II) formation were calculated in the presence and in the absence of oxygen. The results are collected in Tables 2 and 3. There is no significant effect of oxygen on the initial quantum yields. The primary step of the Monuron degradation appears not to be assisted by the oxygen. But oxygen is necessary for the rest of the degradation to obtain the complete mineralisation of the pollutant. As we will see latter, the formation of photoproducts depends on the oxygen concentration.

3.2.2. Kinetics of Monuron degradation and Fe(II) formation

The photoinduced degradation of Monuron in the presence of Fe(III) aquacomplexes was also performed in a reactor with larger volume (60ml) irradiated at 365 nm. First of all, it may be noted that the direct photolysis of Monuron was negligible: no photodegradation of Monuron occurred in the absence of Fe(III). The rate of Monuron disappearance was strongly affected by the concentration of Fe(OH)²⁺. It increased with increasing concentration of Fe(OH)²⁺ (Fig. 1), that is consistent



Fig. 1. Degradation of Monuron upon irradiation at 365 nm of Fe(III) $(3.0 \times 10^{-4} \text{ moll}^{-1})$ /Monuron $(1.0 \times 10^{-4} \text{ moll}^{-1})$ mixtures at various percentage of Fe(III) monomeric species.

with the values of quantum yields. In this set of experiments, the concentration of Fe(II) was also measured all along the transformation (Fig. 2). In all cases Fe(II) was formed, its concentration quickly rose, then reached a plateau value upon continued irradiation. The [Fe(II)] at the plateau is a positive function of the initial concentration of Fe(OH)²⁺. In solution without pollutant, Fe(II) is formed too, but the concentration at the plateau is lower than in the presence of Monuron. In this case, the reaction of oxidation of Fe(II) by OH radicals becomes important: Fe(II) appears to be the major sink of OH radicals (reaction 2) (Buxton et al., 1988):

$$Fe^{2+} + OH \rightarrow Fe^{3+} + OH^- \quad k = 3.2 \times 10^8 \, 1 \text{mol}^{-1} \, \text{s}^{-1}$$
(2)

3.3. Influence of Fe(III) concentration

The photodegradation of Monuron was performed at five different concentrations of Fe(III) aquacomplexes



Fig. 2. Fe(II) formation upon irradiation at 365 nm of Fe(III) $(3.0 \times 10^{-4} \text{ moll}^{-1})/\text{Monuron}$ $(1.0 \times 10^{-4} \text{ moll}^{-1})$ mixtures at various percentages of Fe(III) monomeric species.



Fig. 3. Degradation of Monuron upon irradiation at 365 nm of Fe(III)/Monuron $(1.0 \times 10^{-4} \text{ moll}^{-1})$ mixtures at different Fe(III) concentrations.

 $(1.0 \times 10^{-4}; 3.0 \times 10^{-4}; 1.0 \times 10^{-3}; 1.0 \times 10^{-2} \text{ and } 5.0 \times 10^{-2} \text{ moll}^{-1})$ (Fig. 3). The kinetics of Monuron degradation are strongly dependent on Fe(III) concentration. The disappearance of Monuron became faster when the concentration of Fe(III) increased from 1.0×10^{-4} to $1.0 \times 10^{-3} \text{ moll}^{-1}$. This effect can be correlated with the increase of the monomeric species present in Fe(III) solution. However at highest Fe(III) concentrations, 1.0×10^{-2} and $5.0 \times 10^{-2} \text{ moll}^{-1}$, a decrease of the rate of Monuron disappearance was observed when compared to the kinetics of the reaction with Fe(III) concentration equal to $1.0 \times 10^{-3} \text{ moll}^{-1}$. This negative effect is attributed to two major factors:

- (i) The presence of Fe(III) dimeric species at high concentration of Fe(III) ($\geq 1.0 \times 10^{-2} \text{ moll}^{-1}$). The concentrations of dimeric species were evaluated at 4.5×10^{-4} and 4.2×10^{-3} moll⁻¹ for Fe(III) solution of 1.0×10^{-2} and 5.0×10^{-2} moll⁻¹ respectively, corresponding to 9% and 17% of the total iron respectively. The remaining concentrations of monomeric species were still high $(9.1 \times 10^{-3} \text{ and }$ 4.16×10^{-2} moll⁻¹). However, the dimeric species are the major light-absorbing species at 365nm and the quantum yield of OH radical production is much lower for the dimer than for the monomer Fe(OH)²⁺ (Langford and Carey, 1975; Faust and Hoigné, 1990; Helz et al., 1994) (Table 4). The spectral features associated to the photochemical properties of the dimeric species lead to a negative effect for the elimination of pollutant.
- (ii) The pH of the solution that controls the nature of the Fe(III) monomeric species in solution. The pH of Fe(III) solutions were equal to 2.5 and 1.75 for the concentrations of 1.0×10^{-2} moll⁻¹ and 5.0×10^{-2} moll⁻¹ respectively and the fractions of

Table 4 Spectral and photochemical properties of Fe(III)-hydroxy species (Helz et al., 1994)

Fe(III) species	$(1 \text{mol}^{-1} \text{cm}^{-1})$	$\Phi_{\bullet OH}$
Fe ³⁺	No absorbance at $\lambda > 300 \text{nm}$	ND
Fe(OH) ²⁺	290	$0.017 \ (\lambda = 360 \text{nm})$
$\operatorname{Fe}_2(\operatorname{OH})_2^{4+}$	≈ 5000	0.007 ($\lambda = 350 \mathrm{nm}$)



Fig. 4. Equilibrium speciation of monomeric Fe(III) aquacomplexes at 293K calculated with equilibrium constants given by Faust and Hoigné (1990).

Fe(III) monomeric species, calculated with the equilibrium constants of Fe(III)-hydrolytic equilibrium (Faust and Hoigné, 1990) (Fig. 4), gives 50% and 10% of Fe(OH)²⁺ for pH 2.5 and 1.7 respectively. The remaining of the monomeric species is present as Fe³⁺ species, which do not absorb at wavelength longer than 300 nm and lead also to a negative effect for the elimination of pollutant.

These results illustrate the importance of the speciation of iron in aqueous solution.

3.4. Photoproducts identification and mechanism of degradation

Several peaks appeared in the HPLC chromatogram of an irradiated mixture. The same peaks were observed whatever the percentage of monomeric species. The five major photoproducts were identified (Table 5): two of them by co-injection of the authentic samples synthesised in our laboratory using the procedure proposed by Crosby and Tang (1969). The three other photoproducts were identified by mass spectra analysis and by analogy with the photodegradation studies of dimethylphenylurea derivatives (diuron and chlortoluron) (Mazellier et al., 1997; Poulain et al., 2003). The *N*formyl derivative (IV) was the only photoproduct less

 Table 5

 Structure and mass spectra of the main photoproducts

Number	Molar mass $(M + H)^+$ and ionic fragment	Structure
Ι	215 185, 128	Cl
II	215 187, 144	Cl-V-NH-C-N OH CH3
III	201 144	$CI \longrightarrow OH OH CH3$
IV	Synthesised	Cl-V-NH-C-N CHO
V	Synthesised	

polar than Monuron. Moreover, this N-formyl derivative was observed to be unstable in water solution at room temperature: a moderate reactivity leading to the monomethylated (V) was recorded. The nature of the primary photoproducts can be explained by the reaction of 'OH radicals on two moieties of Monuron: the aromatic ring and the methyl groups of the urea function (cf. mechanism in scheme 1). The two important steps of the mechanism are the formation of the 'OH adduct on the aromatic ring and the abstraction of a hydrogen atom from a methyl group of the dimethylurea function. The OH adduct on the aromatic ring leads to the formation of the hydroxylated photoproduct (II) whereas the radicals formed on the methyl group react with oxygen to form peroxy radical ROO. This radical evolves, through the formation of tetroxide derivative, to alkoxy radical. Different routes (ß scissions and redox reaction with Fe(II)) as described in details by Brand et al. (1998) allow us to account for all the primary identified photoproducts. Afterwards, the mechanism becomes more and more complicated as evidence by the presence of many peaks on the HPLC chromatogram. A nonnegligible thermal reaction (in the dark and at room temperature) is also observed for the conversion of photoproduct I in photoproduct V.

In contrast of the effect on the quantum yield, the absence of oxygen affects the formation of photoproducts. In the absence of oxygen, the carbon centred radical obtained by abstraction of hydrogen by 'OH radical, reacts



Fig. 5. Kinetics of the photoproduct I formation in the absence and in the presence of oxygen. $\lambda_{\rm irr.} = 365 \,\rm nm, \, [Fe(III)] = 3.0 \times 10^{-4} \,\rm mol 1^{-1}$ 90% of monomeric species, [Monuron] = $1.0 \times 10^{-4} \,\rm mol 1^{-1}$.

mainly with Fe(III) aquacomplexes to formed the photoproduct I (alcohol on the methyl group). The formation of alcohol, according to reaction (3), becomes the main pathway (Clark et al., 1988).

$$\mathbf{R}^{\bullet} + \mathbf{F}\mathbf{e}^{3+} \xrightarrow{\mathbf{H}_2\mathbf{O}} \mathbf{R}\mathbf{O}\mathbf{H} + \mathbf{F}\mathbf{e}^{2+} + \mathbf{H}^+$$
(3)

The formation of alcohol is increased by a factor of fifteen in the absence of oxygen (Fig. 5).

In terms of photoproducts, the principal difference between the direct, TiO_2 or iron sensitised photodegradation of Monuron is due to the substitution of the chlorine atom by OH group during the direct photolysis.

3.5. Mineralisation of Monuron

One of the aims of the present work was to test the efficiency of Monuron removal from water solution, when the degradation was photoinduced by Fe(III). Total organic carbon experiment were undertaken in order to make evidence for the complete mineralisation of Monuron. As shown in Fig. 6, the total mineralisation of Monuron was reached after 25h of irradiation with 90% of monomeric species and after 50h with 60% of monomeric species. The complete mineralisation is obtained due to the continuous formation of radical species ('OH). A photocatalytic cycle, in homogeneous phase, based on the couple Fe(III)/Fe(II) and assisted by oxygen (Poulain et al., 2003) is involved. This result also shows that the speciation of Fe(III) (concentration of monomeric species) at the beginning of the irradiation is a very important parameter for the reaction efficiency. A lag period of approximately 10h was observed with 60% of Fe(OH)²⁺. This was due to the formation, accumulation and subsequent degradation of primary organic photoproducts. The lag period was not clearly



Fig. 6. Time evolution of TOC values during irradiation (365 nm) of Fe(III) $(3.0 \times 10^{-4} \text{moll}^{-1}, 60\% \text{ and } 90\% \text{ of monomeric species})/Monuron <math>(1.0 \times 10^{-4} \text{moll}^{-1})$ mixtures.

observed with 90% of Fe(OH)²⁺: this can be explained by the higher rate of the reaction in this case. The evolution of Fe(II) concentration (Fig. 7) is a multistep phenomenon. The very fast formation of Fe(II) at the beginning of the irradiation mainly results from the photoredox process of Fe(OH)²⁺ species. Then Fe(II) concentration reaches a pseudo-constant value (between 7 and 20h of irradiation) corresponding to a photostationary equilibrium between Fe(III) and Fe(II) in the presence of organic compounds. Afterwards, the concentration in Fe(II) decreases and reaches a second plateau value after 25h of irradiation ($\approx 1.2 \times 10^{-4} \text{ mol} 1^{-1}$). This second plateau value corresponds to the photostationary equilibrium between Fe(III) and Fe(II) in the absence of any organic compounds as evidenced by the irradiation of Fe(III) $(3.0 \times 10^{-4} \text{ mol}1^{-1}, 90\% \text{ of}$ $Fe(OH)^{2+}$ alone in aqueous solution (Fig. 7). This result



Fig. 7. Fe(II) and TOC evolutions with and without Monuron for long irradiation times (365 nm) ([Fe(III)] = $3.0 \times 10^{-4} \text{ mol} 1^{-1}$ 90% of monomeric species, [Monuron] = $1.0 \times 10^{-4} \text{ mol} 1^{-1}$).

was confirmed by the correlation with the total organic carbon concentration in solution: the second photostationary equilibrium was reached when the complete mineralisation of the solution was obtained.

4. Conclusions

Our results confirm that Fe(III) can act as an efficient photoinducer of phenylurea herbicides elimination from water solution. Furthermore, photodegradation leads to the complete mineralisation. This work gives evidence for the efficiency of Monuron removal from water by a process of homogeneous photocatalysis providing the continuous formation of 'OH radicals. Moreover, the importance of the speciation of Fe(III) aquacomplexes present in solution was demonstrated for the efficiency of such a process. The use of a high concentration of Fe(III) (> 1.0×10^{-3} moll⁻¹), with the presence of dimeric and Fe^{3+} species, has a negative effect on the degradation of pollutants. As a consequence, the optimum concentrations in Fe(III) necessary in such a process are sufficiently low to make the treated waters compatible with a safe aquatic environment.

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